

(12)

(21) **2 274 649**

(51) Int. Cl. <sup>6</sup>: **H01B 007/28, G02B 006/44**

(22) **10.12.1997**

(85) **10.06.1999**

(86) **PCT/EP97/06887**

(87) **WO98/27559**

(30) **196 52 762.7 DE 18.12.1996**

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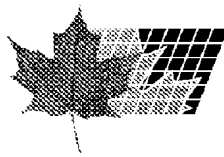
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(54) **COLLE THERMOFUSIBLE SUSCEPTIBLE DE GONFLEMENT**

(54) **SWELLABLE HOT-MELT ADHESIVE**

(57)

Thermoplastic materials on the basis of a water-insoluble constituent of one or more thermoplastic copolymers and one or more resins with a saponification value and a water-soluble or water-dispersible constituent and a water-swellable constituent of the superabsorber class are suitable as water-swellable hot-melt adhesives. Said water-swellable hot-melt adhesives can be preferably used to produce watertight constructions, specially longitudinally watertight cable constructions.



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(51) Int.Cl.<sup>6</sup> H01B 7/28, G02B 6/44  
(30) 1996/12/18 (196 52 762.7) DE  
(54) **COLLE THERMOFUSIBLE SUSCEPTIBLE DE GONFLEMENT**  
(54) **SWELLABLE HOT-MELT ADHESIVE**

(57) Des matières thermoplastiques à base d'un constituant hydro-insoluble d'un ou de plusieurs copolymères thermoplastiques et d'une ou de plusieurs résines avec un indice de saponification, ainsi que d'un constituant hydrosoluble ou hydrodispersible et d'un constituant, susceptible de gonflement dans l'eau, de la classe des superabsorbants conviennent comme colles thermofusibles susceptibles de gonflement en présence d'eau. Ces dernières s'utilisent de préférence pour réaliser des structures étanches à l'eau, notamment des structures de câbles étanches à l'eau dans le sens longitudinal.

(57) Thermoplastic materials on the basis of a water-insoluble constituent of one or more thermoplastic copolymers and one or more resins with a saponification value and a water-soluble or water-dispersible constituent and a water-swellaable constituent of the superabsorber class are suitable as water-swellaable hot-melt adhesives. Said water-swellaable hot-melt adhesives can be preferably used to produce watertight constructions, specially longitudinally watertight cable constructions.



**PCT**WELTORGANISATION FÜR GEISTIGES EIGENTUM  
Internationales BüroINTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE  
INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

<b>(51) Internationale Patentklassifikation <sup>6</sup>:</b>  <b>H01B 7/28, G02B 6/44</b>	<b>A1</b>	<b>(11) Internationale Veröffentlichungsnummer:</b> <b>WO 98/27559</b>  <b>(43) Internationales Veröffentlichungsdatum:</b> 25. Juni 1998 (25.06.98)
<b>(21) Internationales Aktenzeichen:</b> PCT/EP97/06887 <b>(22) Internationales Anmeldedatum:</b> 10. Dezember 1997 (10.12.97)  <b>(30) Prioritätsdaten:</b> 196 52 762.7 18. Dezember 1996 (18.12.96) DE  <b>(71) Anmelder:</b> HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN [DE/DE]; Henkelstrasse 67, D-40589 Düsseldorf (DE).  <b>(72) Erfinder:</b> BUTTERBACH, Rüdiger; Neckarstrasse 56, D-45219 Essen (DE). MAASSEN, Ulrike; Neuenbergerstrasse 44, D-41470 Neuss (DE). KOPANNIA, Siegfried; Ringofenweg 3, D-47809 Krefeld (DE). HEEMANN, Marcus; Witzelstrasse 20 a, D-40225 Düsseldorf (DE).		<b>(81) Bestimmungsstaaten:</b> BR, CA, JP, NO, europäisches Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Veröffentlicht</b> <i>Mit internationalem Recherchenbericht.          Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist. Veröffentlichung wird wiederholt falls Änderungen eintreffen.</i>
<b>(54) Title:</b> SWELLABLE HOT-MELT ADHESIVE  <b>(54) Bezeichnung:</b> QUELLBARER SCHMELZKLEBSTOFF  <b>(57) Abstract</b>  Thermoplastic materials on the basis of a water-insoluble constituent of one or more thermoplastic copolymers and one or more resins with a saponification value and a water-soluble or water-dispersible constituent and a water-swellable constituent of the superabsorber class are suitable as water-swellable hot-melt adhesives. Said water-swellable hot-melt adhesives can be preferably used to produce watertight constructions, specially longitudinally watertight cable constructions.  <b>(57) Zusammenfassung</b>  Thermoplastische Massen auf der Basis einer nichtwasserlöslichen Komponente aus einem oder mehreren thermoplastischen Copolymeren und einem oder mehreren Harzen mit einer Verseifungszahl sowie einer in Wasser löslichen oder wasserdispergierbaren Komponente und einer in Wasser quellbaren Komponente aus der Klasse der Superabsorber eignen sich als mit Wasser quellbare Schmelzklebstoffe. Derartige mit Wasser quellbare Schmelzklebstoffe finden bevorzugte Anwendung zur Herstellung wasserdichter Konstruktionen, insbesondere zur Herstellung längswasserdichter Kabelkonstruktionen.		

**A b s t r a c t**

Thermoplastic compositions based on a water-insoluble component of  
5 one or more thermoplastic copolymers and one or more resins with a  
saponification number and a water-soluble or water-dispersible component  
and a water-swellaable component from the class of superabsorbers are  
suitable as water-swellaable hotmelt adhesives. Such water-swellaable hotmelt  
adhesives are preferably used for the production of watertight constructions,  
10 more particularly for the production of longitudinally watertight cable  
constructions.

## **A Swellable Hotmelt Adhesive**

### **Field of the Invention**

This invention relates to a water-swellable thermoplastic bonding and coating composition based on a water-insoluble component, a water-soluble  
5 or water-dispersible component and a water-swellable component. The invention also relates to the use of this thermoplastic composition for the production of watertight constructions, more particularly for the production of longitudinally watertight cable constructions.

### **Background of the Invention**

10 A number of constructions, for example pipelines and, in particular, underground or underwater cables, have to be protected against penetrating water at junctions and joints or in the event of damage to their outer casings. Power and/or telecommunications cables in particular are long-life capital goods whose reliability has to be guaranteed over a very long period. In the  
15 event of damage to the outer insulation and/or at faulty junctions, water penetrates into such cable constructions and can cause serious damage to the cable. Water can spread rapidly along the cable so that a cable damaged in this way can become unusable over long stretches.

To prevent water from penetrating into such constructions, it has been  
20 common practice for some time to use water-swellable sealing materials or sealing constructions. **JP-A-58-215334 (83)** describes in general terms heat-curing sealing materials based on rubbers and a water-swellable polyurethane resin based on ethylene oxide/propylene oxide copolymers.

According to the prior art, multilayer sealing systems are used for the  
25 production of longitudinally watertight power and telecommunications cables.

Thus, in "**Draht und Kabelpanorama**", **May/June/July 1988**, W. Schäfer and P. Graber describe swellable "nonwovens" of an extremely homogeneous swelling layer, consisting of a mixture of a synthetic hydrogel former (swelling  
30 powder) with chemically pure cellulose pulp as filler, and a high-strength carrier layer of polyester fibers with polyester filaments as an additional reinforcing element. These two layers are thermally united solely by applying

heat and high pressure, i.e. without using low-melting thermoplastics. Swellable bandages are then made from these nonwovens or yarns and wrapped around the bundle of wires, optionally together with an inner plastic sheath.

5           **EP-A-188 959** describes a multilayer sealing tape consisting of a support of paper, textiles or plastics which is coated with a layer of a water-swellable polymeric powder and a water-soluble binder and optionally a surfactant.

**US-A-5,020,875** describes cable constructions in which the layer  
10 intended to keep water out by swelling consists of a multilayer laminate. This laminate consists of two support tapes of a hydrophobic material, for example polyester. A water-swellable polymer or copolymer of the superabsorber type is arranged between these two support tapes.

**US-A-5,188,883** describes a multilayer composite structure of a metal  
15 tape as one layer and a layer of a swellable water-blocking material, these two layers and surfaces being joined by an adhesive.

          The use of the multilayer materials mentioned above for the production of longitudinally watertight cable constructions is complicated and expensive on account of the number of steps involved. Accordingly, the problem  
20 addressed by the present invention was to provide products which would enable longitudinally watertight cable constructions to be more simply produced.

#### **Summary of the Invention**

          According to the invention, this problem has been solved by a water-  
25 swellable thermoplastic composition which consists essentially of three components:

- A.) a water-insoluble component containing at least one water-insoluble polymer or copolymer and at least one other substantially water-insoluble resin,
- 30 B.) a water-soluble or water-dispersible component containing at least one water-soluble or water-dispersible oligomer and/or polymer or

copolymer,

C.) a water-swellaable component consisting of a water-swellaable homopolymer or copolymer,

components A, B and C being homogeneously mixed. "Homogeneously

5 mixed" in the context of the present invention is supposed to mean that the matrix of the composition has no macroscopic inhomogeneities. This does not imply that different phases consisting of the water-insoluble component and the water-soluble or water-swellaable component are present in the microscopic range. More particularly, homogeneously mixed is not intended  
10 to mean that the water-swellaable homopolymer or copolymer of component C is molecularly dissolved in one or both of the other components.

Accordingly, these water-swellaable thermoplastic compositions are hotmelt adhesives which may be used in particular in cable constructions.

#### **Brief Description of the Drawings**

15 Figure 1 is a schematic cross-section through an optical cable using the swellaable hotmelt adhesives of one embodiment of the invention.

#### **Detailed Description of the Invention**

Basically, the water-insoluble homopolymer or copolymer of component A may be selected from any thermoplastic polymers known per se for use in hotmelt adhesives including, for example, polyamides, copoly-  
20 amides, polyaminoamides, polyesters, polyacrylates, polymethacrylates, polyolefins and, in particular, ethylene/vinyl acetate copolymers or mixtures of one or more of the polymers mentioned.

Any tackifying resins known per se except for pure hydrocarbon resins  
25 may be used as an additional resin of component A to increase the tackiness of the melt. Accordingly, the resins to be used in accordance with the invention have a saponification number different from 0. The various colophony derivatives, i.e. in particular the resin esters of abietic acid, are particularly suitable for this purpose although other polyterpenes and terpene/  
30 phenol resins may also be used.

Various water-soluble or water-dispersible oligomers or homopolymers

or copolymers are suitable for the constituents of component B, including for example polyethylene glycols with molecular weights of 400 to 20,000, polyvinyl methyl ether, polyvinyl pyrrolidone, copolymers of vinyl methyl ether or vinyl pyrrolidone, polyvinyl alcohols, water-soluble or water-dispersible  
5 polyesters or copolyesters, water-soluble or water-dispersible acrylate polymers.

The water-swellaable component C may be selected from any homopolymers and/or copolymers which, as hydrophilic materials, are capable of absorbing and retaining large amounts of water, even under  
10 pressure, without immediately dissolving in the water. Hydrophilic materials such as these are also known as "superabsorbers" and include, for example, graft copolymers of starch or cellulose with acrylonitrile, acrylic acid or acrylamide, carboxymethyl cellulose, maleic anhydride/poly- $\alpha$ -olefin copolymers, polyacrylamide, polyacrylic acid and salts of polyacrylic acid and  
15 optionally copolymers of acrylic acid or acrylamide with acrylate esters.

Depending on the application envisaged, the hotmelt adhesives according to the invention may have surface-tacky properties or tack-free surfaces for so-called "non-blocking" versions. These particular versions contain wax additives known per se, more particularly bis-stearamide waxes.  
20 In addition, both versions of the hotmelt adhesives according to the invention may contain commercial stabilizers known per se which provide the formulations with thermal stability.

Particularly preferred surface-tacky swellaable hotmelt adhesive compositions contain the following components:

- 25 15 to 45% by weight of resin esters or terpene/phenol resins,
- 15 to 40% by weight of thermoplastic copolymer, more particularly ethylene/vinyl acetate copolymer,
- 5 to 20% by weight of acrylate copolymers,
- 5 to 30% by weight of polyethylene glycols,
- 30 5 to 15% by weight of polyvinyl ethyl ethers, water-soluble or water-dispersible acrylate polymers or water-soluble or water-dispersible



copolyesters,

15 to 50% by weight of powder-form polyacrylic acid salt, polyacrylamide or similar powder-form superabsorbers,

0.2 to 2.0% by weight of commercial stabilizers.

5            Particularly preferred swellable hotmelt adhesive formulations in the non-blocking version contain:

15 to 45% by weight of resin esters, terpene/phenol resins or the like,

15 to 40% by weight of thermoplastic (co)polymer, more particularly ethylene/vinyl acetate copolymer,

10          5 to 25% by weight of polyethylene glycols,

15 to 50% by weight of powder-form superabsorbers, more particularly polyacrylic acid salt,

0.2 to 2.0% by weight of stabilizer,

0.5 to 5.0% by weight of waxes, more particularly ethylene bis-stearamide.

15            The water-swellaible hotmelt adhesives according to the invention are suitable, for example, as a coating for metal foils or glass-fiber-reinforced plastic reinforcing elements in cable constructions. A particularly preferred application, for example, is the direct coating of the central reinforcing element in optical cables. This central element may be coated with the non-  
20          surface-tacky version of the adhesive and then rolled up and stored. In standard optical cables, the individual optical fibers are arranged concentrically around this central element. After reactivation of the non-surface-tacky version of the adhesive on the central element, the optical fibers may be directly bonded to the central element and may then pass through  
25          further stages of the production process. The plastic tubes containing the optical fiber(s) may optionally be externally coated with the hotmelt adhesive according to the invention. The hotmelt adhesives according to the invention eliminate the need for the otherwise necessary wrapping of the optical fibers in a water-swellaible multilayer adhesive tape or multilayer non-woven and the  
30          additional longitudinal waterproofing of the voids between the central element and the tubes with a petrojelly. These voids which arise out of the design of

the cable construction can be left in the construction because the water-swella-  
ble hotmelt adhesive completely fills them whenever water penetrates  
and triggers the swelling process, so that reliable longitudinal waterproofing  
is guaranteed. This type of construction simplifies cable splicing, eliminates  
5 the need for petrojelly and significantly reduces the weight of the cable. In  
addition, higher production speeds are possible compared with swelling yarns.

In the surface-tacky version, the hotmelt adhesive according to the  
invention is directly applied to the central element and/or the optical fiber in  
the cable construction line so that the hotmelt adhesive does not have to be  
10 reactivated in this case.

Figure 1 is a schematic cross-section through an optical cable using  
the swellable hotmelt adhesives according to the invention. The central  
element 1 is surrounded by several tubes 2 containing optical fibers. A  
coating 3 of the swellable hotmelt adhesive around the optical fibers is shown.  
15 The cable sheath 4 seals off the cable from the outside.

The invention is further described by the following example which is  
not to be construed as limiting.

#### **Example**

The water-swella-ble hotmelt adhesives are produced as follows:  
20 Resin ester, ethylene/vinyl acetate and acrylate copolymer are melted  
and homogenized at 140 to 160°C. The polydiol(s) is/are then added and  
homogenized. The polyvinyl methyl ether and the stabilizer are then added  
and homogenized. Lastly, the powder-form polyacrylic acid salt is added and  
homogenized. In the non-blocking versions, the wax is added and  
25 homogenized last. The homogeneous melt is then introduced into  
appropriate containers and cooled to room temperature.

The dependability of the water-swella-ble hotmelt adhesive is  
established by the following test:

Both sides of a 0.1 mm thick polyester film are coated with the hotmelt  
30 adhesive in a thickness of 0.2 mm to at most 0.4 mm. The total layer  
thickness of the coated film should not exceed 1 mm. The film coated on both

sides is wrapped around a Teflon rod (200 mm long, 19 mm in diameter) with a maximum overlap of 2 mm at the longitudinal seam. A glass tube with an internal diameter of 23 mm and a length of 350 mm is provided with a loose cottonwool plug at its lower end, after which the Teflon rod wrapped in the coated film is inserted into the middle of the glass tube and the upper end of the vertical glass tube is closed with another loose cottonwool plug. Arranged above the glass tube is a dropping funnel containing 250 ml of deionized water.

If the water is allowed to drip slowly into the glass tube from above, the hotmelt adhesive quickly swells to such an extent that only a few ml of water are able to flow out from the lower end of the glass tube during a brief initial phase. Thereafter there is no further penetration of water.

The water-swellable hotmelt adhesive used for the above test had the following composition:

- 15 19.5 parts of pentaerythritol ester of abietic acid
- 29.8 parts of ethylene/vinyl acetate
- 10.0 parts of a copolymer of ethylene, acrylic acid, vinyl acetate and vinyl alcohol
- 0.2 part of sterically hindered phenol as antioxidant
- 20 19.5 parts of polyethylene glycol, molecular weight 12,000
- 20.0 parts of the sodium salt of polyacrylic acid (swelling agent)
- 1.0 part of ethylene bis-stearamide (antiblocking agent).

## Article 34 Amendment

8

**CLAIMS**

1. A water-swellaable hotmelt based on
  - A.) a water-insoluble component,
  - B.) a water-soluble or water-dispersible component and
  - C.) a water-swellaable component,characterized in that component A contains at least one water-insoluble (co)polymer and at least one other resin, component B contains at least one water-soluble or water-dispersible oligomer and/or (co)polymer and component C consists of a water-swellaable (co)polymer, components A, B and C being homogeneously mixed.
2. A hotmelt adhesive as claimed in claim 1, characterized in that component A contains one or more resins with a saponification number, at least one thermoplastic (co)polymer and optionally tackifying additives.
3. A hotmelt adhesive as claimed in claim 1, characterized in that component A contains one or more resins with a saponification number, at least one thermoplastic (co)polymer and tack-reducing additives.
4. A hotmelt adhesive as claimed in claims 1 to 3, characterized in that the water-swellaable (co)polymer of component C is a superabsorber from the group consisting of polyacrylic acid, polyacrylic acid salts, polyacrylamide or copolymers thereof, optionally with acrylonitrile, or graft polymers or copolymers of the above-mentioned group with starch or cellulose.
5. A hotmelt adhesive as claimed in claims 1 to 4, characterized in that the water-soluble or water-dispersible oligomer/(co)polymer of component B is selected from the group consisting of polyethylene glycol, polyvinyl methyl ether, polyvinyl pyrrolidone, water-soluble or water-dispersible polyesters or copolyesters, water-soluble or water-dispersible acrylate polymers.
6. The use of the water-swellaable hotmelt adhesive claimed in at least one of the preceding claims as a hotmelt adhesive and sealant or coating composition for the production of watertight constructions, more particularly for the production of longitudinally watertight cable constructions.

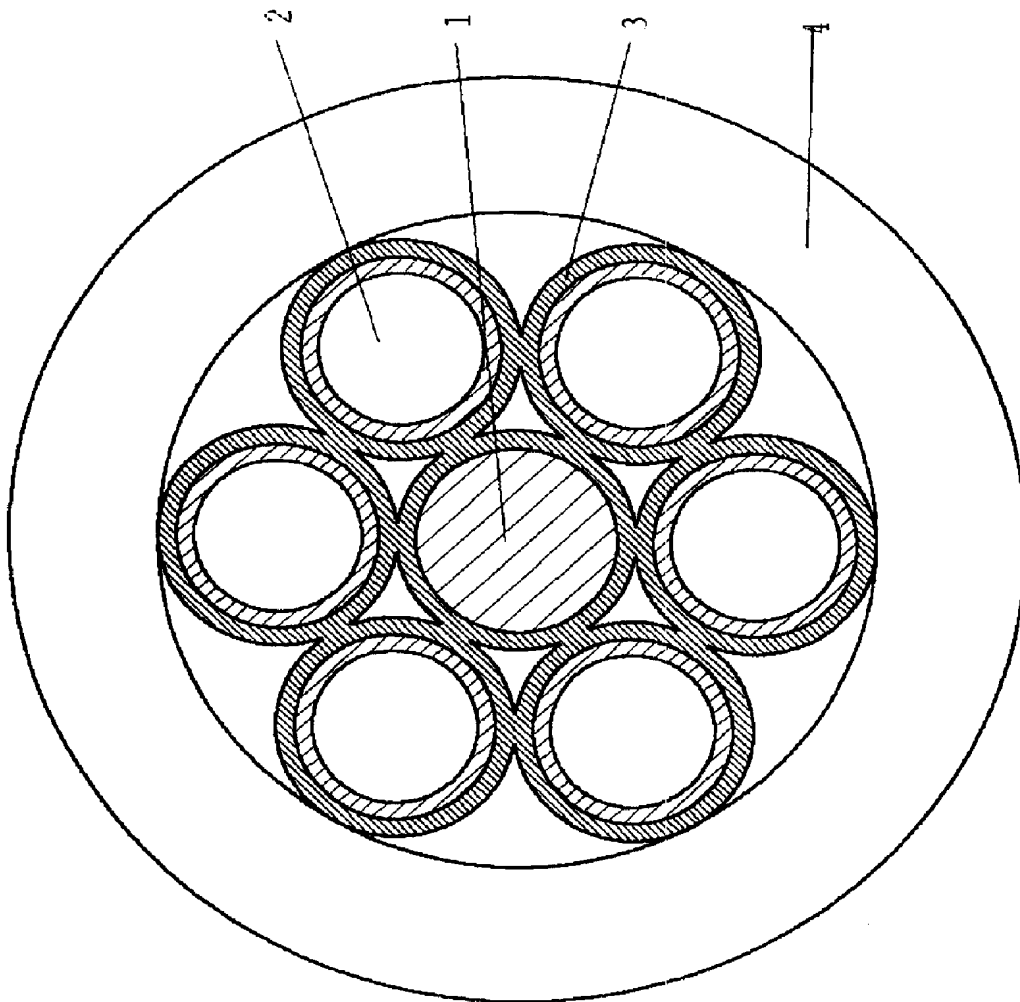


Fig.1